PSEUDOMORPHIC AND RELAXED GeSi:Si HETEROSTRUCTURES FORMED BY ION IMPLANTATION FOR HETEREPITAXIAL TEMPLATES

O. W. Holland, K. Hossain, and T. D. Golding*
University of North Texas, Department of Physics, Denton, TX, 76203

M. F. Chisholm
Oak Ridge National Laboratory, Oak Ridge, TN, 37831

ABSTRACT

A method of forming Ge_xSi_{1-x} films by thermal oxidation of Ge^+-implanted Si is presented. The process involves the segregation of the implanted Ge during oxidation to form a distinct Ge-rich layer at the oxide interface. The composition of the segregated layer can be altered by varying the oxidation conditions as a result of the kinetic competition between oxidation and the interdiffusion of the segregated layer with the underlying Si substrate. Rutherford backscattering results show that the Ge-rich layer becomes more dilute at higher oxidation temperatures. Below a critical thickness, the segregated film forms pseudomorphically on the underlying Si. However, the observed critical thickness greatly exceeds the value predicted (Matthews et. al., 1974) for pseudomorphic growth. Dislocation-free relaxation of the Ge_xSi_{1-x} films formed within a Si-on-insulator (SOI) wafer is achieved with a unique vacancy-injection technique. The encapsulation of the segregated film by the oxide layers in the SOI ensures that the injected vacancies remain within the volume of the film to relax the strain and are not lost to the underlying substrate.

1. INTRODUCTION

Heterojunctions have dramatically improved the performance and functionality of semiconductor devices. However, there now exists a wide range of incompatible device technologies. Integrated circuits (IC's) are primarily Si-based, while high performance RF devices, optical sources and detectors are typically based on III-V and II-VI material systems. In each device the rigorous demands on material quality currently require that the device structure be grown epitaxially on a lattice matched, or a near lattice matched, template to avoid performance degradation. The "Holy Grail" of optoelectronics is to integrate III-V's, II-VI's and Si on a single platform to provide both optical and digital functionality. In addition, pseudomorphic Si:Ge_xSi_{1-x} heterostructures have been shown to exhibit large increases in carrier mobility within the compressively-strained layer. The ability to form oriented germanium-rich films (e.g. fully relaxed and dislocation-free) on Si enables both the integration of GaAs, as well as Ge_xSi_{1-x} heterostructures over a wide compositional range. It has previously been demonstrated that Ge is totally rejected during thermal oxidation of Ge^+-implanted Si (Holland et. al., 1987; Fathy et. al., 1987). This segregation produces a 'snow-plow' effect that forms a high concentration of Ge at the Si/SiO_2 interface. The concentration profile depends upon the kinetic competition between the segregation effect during oxidation that piles up the Ge at the interface, and interdiffusion of the Ge-rich layer with the underlying Si substrate. This competition depends upon the oxidation conditions (i.e. oxidant and temperature) and can be adjusted to yield either a highly enriched Ge layer, or a Ge_xSi_{1-x} film of arbitrary composition. It has also been reported that the presence of a Ge-enriched layer at the oxide interface enhances oxidation kinetics in a wet ambient (Holland et. al., 1987; Fathy et. al., 1987, Terrasi et. al., 2002) and dry conditions with some ambiguities (LeGoues et. al., 1989, Spadafora, et. al., 2003). The Ge layer forms pseudomorphically on the underlying substrate with a thickness that greatly exceeds the critical thickness as predicated by equilibrium models (Matthews et. al., 1974). In this paper, a method of achieving relaxation of this film without plastic deformation will be presented. It depends upon application of this unique process of forming a Ge_xSi_{1-x} film in a silicion-on-insulator (SOI) wafer rather than bulk Si. It should be noted that a number of studies have reported some degree of relaxation of pseudomorphic films on oxide substrates. Hobart (Hobart et. al., 2000) reported relaxation in a compressively strained SiGe film bonded to a borophosphorosilicate glass by buckling, which could be avoided by patterning the film into small areas prior to annealing (i.e. relaxation). Furthermore, modification of relaxation behavior has been observed in lattice-mismatched films due to growth on a 'compliant' substrate consisting of a thin template layer on an oxide substrate (Moran et. al., 2000). Effects include a reduced dislocation density of films greatly exceeding their (Matthews-Blakeslee) critical thickness (Powell et. al., 1994, Chu et. al., 1997, Yang et. al., 1998), as well as a much narrower strain distribution and a smaller rms roughness (Moran et. al., 1999) (compared to films grown on conventional substrates).

The critical part of the process is the relaxation of these thin films without forming misfit dislocations. This involves the use of a silicon-on-insulator (SOI) substrate, which allows the Ge-rich film to be transported to the buried oxide interface during thermal oxidation of the

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14. ABSTRACT

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superficial Si layer. Relaxation of the segregated film is then achieved by injection of vacancies to provide sufficient open volume within the lattice to accommodate the compressive strain. An ion beam process is discussed which is used to inject vacancies in sufficient numbers to produce either full or partial relaxation of the strain. Characterization of the films formed by this method will be discussed as well as methods to achieve pseudomorphic and relaxed structures.

2. EXPERIMENTAL

Commercially-available, bonded SOI wafers provided by SOITEC Inc. were used in this study. The SOI wafers were implanted at ambient temperature with a dose of 5×10^{16} Ge^{+}-ions/cm^2 at an energy of 80 keV. Prior to oxidation, the implanted wafers were cleaned using a diluted HF solution (1:1 = 48% HF: DI water) followed by rinsing with DI water to remove any impurities and/or native oxides. Oxidation was done in a standard quartz-tube furnace under flowing dry O_2. As described later, the oxide layer was removed for a variety of purposes. In those cases, the oxide was carefully stripped off using a dilute HF-treatment. Care was exercised to ensure that none of the underlying Ge was removed during this process.

Rutherford backscattering channeling spectrometry (RBS) was used for measuring the thickness of the grown oxide layers and the composition of the Ge_xSi_{1-x} films. The RBS measurements were done using 1.5 MeV He^+ ions with a detector located at a scattering angle of 135°. Spectral simulation generated by a standard computer code, SIMNRA (Mayer et. al., 1999), was used to determine sample parameters that yielded a best fit to the experimental data.. Thus, parameters such as composition of the Ge_xSi_{1-x} layers and the oxide thickness were determined from the fit parameters used in the simulated spectrum. Lattice strain was measured by x-ray diffraction (XRD) techniques and cross-sectional, transmission electron microscopy, XTEM) was used to evaluate the detailed microstructure in the samples.

3. RESULTS AND DISCUSSION

The segregation of the implanted Ge is demonstrated in Fig. 1 by RBS spectra comparing two implanted samples oxidized at 950°C for two different times. Simulated spectra are also shown and were calculated assuming that the sample consisted of a SiO_2:Ge_xSi_{1-x}:bulk Si multilayer. The good agreement with the data clearly indicates that the Ge is completely segregated at the oxide interface. Also, the arrows in the spectra mark the location of scattering from Si and O atoms at the surface of the oxide. It is clear that scattering from the oxide indicates that the oxide thickness after 30 minutes is much larger than at 5 minutes, as expected. The presence of a surface oxide is also seen in the scattering profile from the Si portion of the spectra. The peaks in each spectrum, located at a scattering energy beyond the Si edge are the result of scattering from Ge in the samples. The different peak positions indicate that the Ge is located deeper within the sample with the thicker oxide. As discussed earlier, the position of the peaks is consistent with the location of the Ge layer at interface between the oxide and underlying Si.

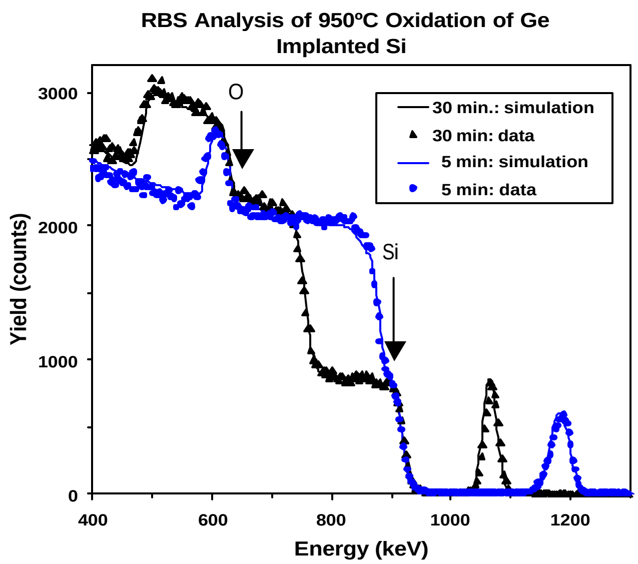


Fig. 1. RBS spectra from Ge-implanted Si oxidized at 950°C in wet conditions for 5 and 30 minutes respectively. Simulated spectra using SIMNRA are also shown.

RBS spectra in Fig.2 provide a comparison of the composition of the segregated Ge_xSi_{1-x} layers in implanted samples oxidized at different temperatures. The spectra were acquired using a scattering geometry chosen to maximize the depth resolution of the measurements. A best-fit simulated spectrum is shown for each of the different experimental conditions. The results show that the sample oxidized at 900°C results in the formation of an almost pure-100% Ge film while the composition of the film decreases to only 30% Ge in the sample oxidized at 1050°C. This clearly demonstrates that the process is capable of forming thin Ge_xSi_{1-x} films over a wide compositional range.

Fig. 3 shows an XTEM of a 5 nm thick Ge film formed on Si(100) by implantation (80 keV, 2×10^{16}cm^{-2}) and wet oxidation (O_2 bubbled thru 95°C H_2O). This film is seen to be pseudomorphic with a thickness 3-6× greater than critical thickness of a Ge:Si heterostructure grown by molecular beam epitaxy (MBE). This is believed to be the result of differences in the two techniques. First the segregated film is capped by an

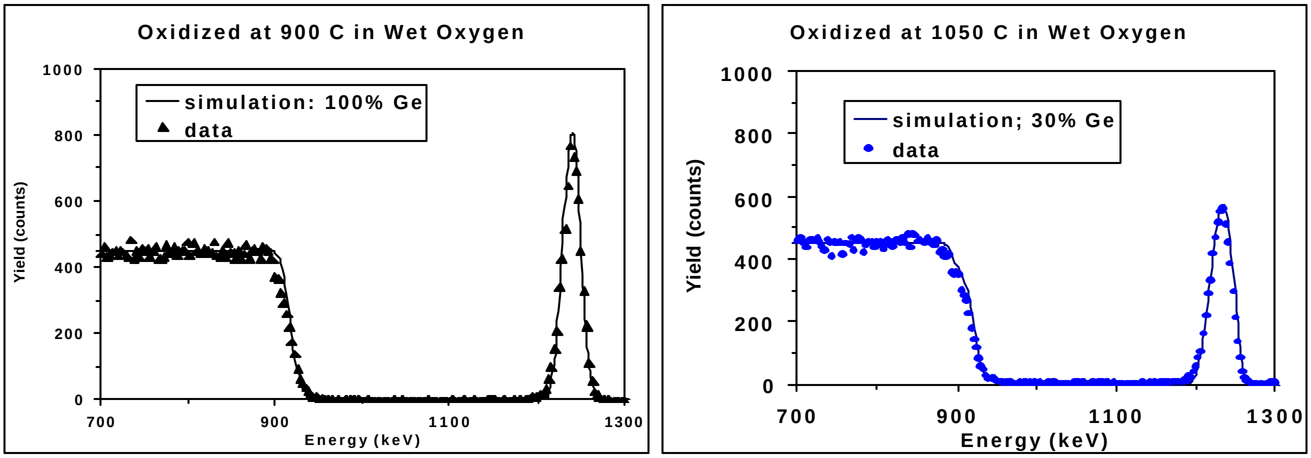


Fig. 2. Comparison of RBS spectra acquired from Ge^+-implanted Si after oxidation at 900°C and 1050°C. Composition is determined by the best-fit simulated spectra shown for each spectral condition.

oxide layer and forms layer-by-layer, whereas MBE growth occurs by islanding.

The process to produce a relaxed Ge film begins with the use of SOI (rather than bulk Si) to decouple the Ge

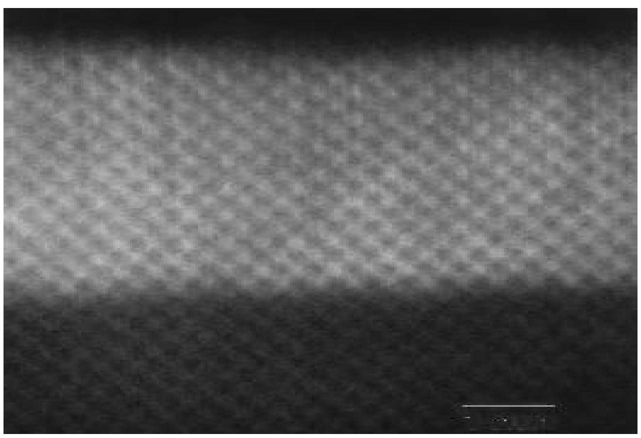
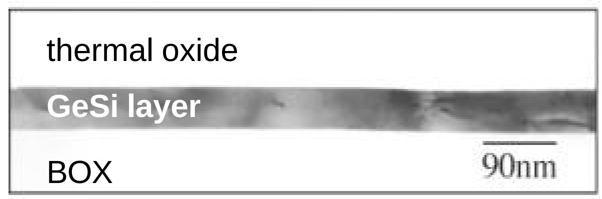
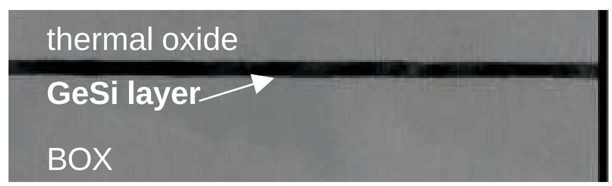


Fig. 3. High-resolution, XTEM of Ge^+-implanted (80 keV, $2x10^{16}cm^{-2}$) Si after wet oxidation at 900°C/1hr.

layer from the Si substrate. The SOI material consisted of a 200 nm buried oxide layer (BOX) beneath a 200 nm superficial Si layer. The buried oxide interface is used to form an incommensurate boundary with the segregated Ge film. The process was accomplished by oxidizing a Ge^+-implanted Si to remove the Si from the top layer. Oxidation continued until enrichment of the top layer produced the GeSi layer shown in Fig. 4a. The bright field image reveals a misfit dislocation array near the centerline of the film with some threading segments going to the top and others going to the bottom surface. XRD determined that the formation of the dislocations had resulted in a partial relaxation of the film. It is clear that viscoelastic response of the oxide substrate is insufficient to prevent plastic deformation of a blanket film on oxide as reported elsewhere (Hobart et. al., 2000).



(a) GeSi layer formed in SOI relaxed by formation of misfit dislocations.



(b) $Ge_{0.7}Si_{0.3}$ layer formed in SOI using vacancy injection to relax strain.

Fig. 4. (a) XTEM of dry oxidation @ 1150°C/4 hrs. of Ge^+-implanted SOI showing the Ge-rich segregated layer encapsulated by the top thermal oxide and the buried oxide (BOX). Dislocations are clearly seen. (b) XTEM of sample similarly prepared as in (a) except strain relaxed by vacancy injection using a Si^+-ion beam.

Alternatively, vacancy injection into the film was attempted to provide sufficient open volume within the lattice to accommodate the compressive strain. Ion irradiation with sufficient energy to penetrate through a layer has been shown to inject an excess of vacancies into the layer (Holland et. al., 1998). If the injected vacancies remain within the layer, they can induce a collective response to promote atomic rearrangements needed to restore equilibrium lattice site occupation. Therefore, vacancies were injected into the samples prior to plastic deformation of the film. This was done using 210 keV Si^+-ions at sufficient numbers (10^{16} cm^{-2}) to accommodate

most of the strain. Subsequent to this irradiation, the oxidation of the sample was continued to consume the remaining Si encapsulated between the oxide layers as shown in Fig. 4b. XTEM inspection of the irradiated layer revealed that it had a composition of ~70% Ge and was dislocation-free (within the entire field of view in the microscope). XRD measurement indicated that the film was substantially relaxed, i.e. >60%. Since the film is continuous with no evidence of void formation, the action of the injected vacancies must have been to promote movement of the atoms onto equilibrium sites.

The injection of vacancies into a film by ion irradiation is a well-understood phenomena (Holland et. al., 1998, Kalyanaraman et. al., 2001, Kalyanaraman et. al., 2002). It depends mainly upon the differences in the transport of interstitials and vacancies during ion-induced Frenkel pair production. Simulation of the ion-atom interaction in solids can be done with a computer code known as SRIM (Ziegler). This code tracks the interstitial transport in the solid within ion cascades, and as such can be used to determine the vacancy injection rate. As discussed, vacancy injection can be more accurately described by interstitial transport. Simulation results showing the excessive vacancies within a Ge film within a $Si:Ge:SiO_2$ heterostructure is shown in Fig. 5. The data denoted as Ge atoms gives the depth dependent change in the atomic density of Ge.

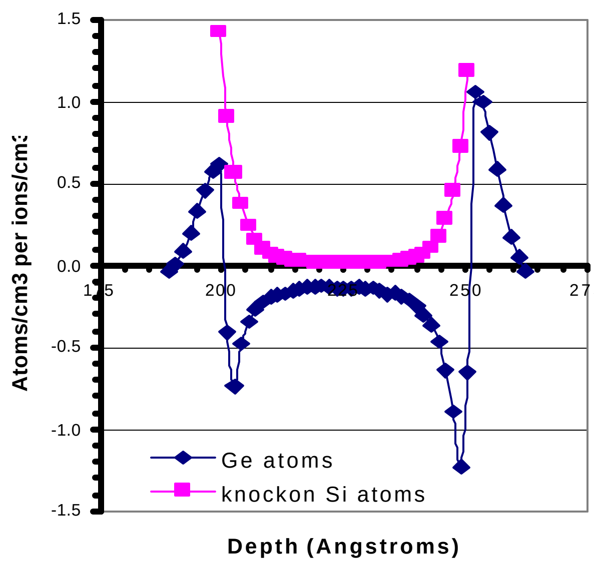


Fig. 5: Simulation of rarefaction of Ge in a $Si:Ge:SiO_2$ heterostructure by irradiation with 80 keV Ge^+-ions.

It can be seen that within the boundaries of the Ge layer that there has been a substantial loss of Ge atoms, i.e. vacancy injection. It is this injection of open volume that provides the driving force for a compressively strained layer to relax.

4. CONCLUSION

A method of forming a thin Ge_xSi_{1-x} film involving Ge^+-implantation and thermal oxidation has been demonstrated. The formation nominally results in a biaxially-strained heterostructure. A novel method of strain relaxation was demonstrated when the thin film process is done in SOI. Vacancy injection by ion irradiation through the layer results in the introduction of open volume into the compressively strained region providing a pathway for relaxation without plastic deformation.

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